Thermodynamics, Solubility and the Separation of Uranium from Cerium in Molten In/3LiCl-2KCl System

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Thermodynamics, Solubility and the Separation of Uranium from Cerium in Molten In/3LiCl-2KCl System

Minghui Xu,[1,2] Valeri Smolenski,[1,3,4] Qi Liu,[1] Alena Novoselova,[1,3,4,z] Kewei Jiang,[1,2] Jing Yu,[1] Jingyuan Liu,[1] Rongrong Chen,[1] Hongsen Zhang,[1] Milin Zhang,[1] and Jun Wang[1,2,5,z]

[1]*Key Laboratory of Superlight Material and Surface Technology, Ministry of Education, Harbin Engineering University, Harbin 150001, People's Republic of China*
[2]*College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, People's Republic of China*
[3]*Institute of High-Temperature Electrochemistry UB RAS, Ekaterinburg 620990, Russia*
[4]*Department of Rare Metals and Nanomaterials, Institute of Physics and Technology, Ural Federal University, Ekaterinburg 620002, Russia*
[5]*Harbin Engineering University Capital Management Co. Ltd., Harbin 150001, People's Republic of China*

The purpose of this work is to study the electrochemical behavior of uranium and cerium in fused In/3LiCl-2KCl system in the temperature range of 723–823 K by open-circuit potentiometry. The apparent electrode potential of Ce^{3+}/Ce (U^{4+}/U) couples and apparent standard potential of Ce-In (U-In) alloys vs AgCl/Ag reference electrode were established. The principal thermodynamic properties, activity and solubility of cerium and uranium were determined. The separation factor of uranium/cerium couple on liquid indium electrode was calculated. The experimental results have been shown that a lower temperature should be more effective for the separation uranium from cerium.
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Nuclear power is one of the most environmentally friendly sources of electricity compared to existing ones that use coal and gas. Today, it plays an increasingly important role in the development of modern society. The emergence of nuclear power gives us the confidence when we talk about the replacing of organic fuel with nuclear fuel. However, the development of nuclear power will also lead to the increasing of radioactive waste. Currently, the efficient reprocessing of spent nuclear fuel (SNF) is becoming the most actual problem in the world.[1–3]

At recent years electrolysis or extraction in molten salts has been increasingly used for reprocessing of nuclear waste. Molten salts is used as a solvent during the high-temperature thermochemical treatment of SNF because of their good chemical and radiation stability. Facts have proved that molten salts are feasible as a reaction medium in the process of separating lanthanides (Ln) and actinides (An), which is also the most promising research plan for the treatment of radioactive waste and spent nuclear fuel.[4–6] Today, the most important issue for reprocessing of spent nuclear fuel is a creation of closed fuel cycle. Therefore, the separation and extraction of nuclear fission products have become one of the most important issues in the world nuclear industry today.[6–10]

Currently, high-temperature methods are being studied for reprocessing highly enriched SNF with a short holding time in liquid metal-molten salt systems. For this it is necessary to study the electrochemical properties and behavior of both rare earth elements and basic fuel components (U, Pu). The nature and the composition of the studied molten system plays a determining role for the selectivity separation process of fission products.[8,9,11–28] Understanding of the thermodynamic properties of fission elements in SNF is critical to practical applicability in the actual separation process. Cerium is one of the most dangerous elements of fission products and, in addition, is a neutron poison. The electrochemical and thermodynamic properties of cerium chloride compounds in molten 3LiCl-2KCl eutectic were investigated at different temperatures. The data show one-step reduction reaction of Ce (III) ions to metal occurs on inert solid electrode. Also, it has been determined one-step reduction process on active liquid electrodes by transient electrochemical technique.[29–33] The electrochemical and thermodynamic properties of uranium compounds in molten 3LiCl-2KCl eutectic were studied.[11,34–37] The mechanism of cathodic reduction of uranium ions to metal and the influence of various factors on this process has been investigated in these works. The thermodynamic properties of the formation of An and Ln intermetallic compounds on liquid electrodes, including the solubility in the liquid metals, the activity coefficients, the separation factor between the An and Ln, and the Gibbs free energy change have been studied. Although the separation of fission elements on liquid electrodes is very effective and promising, there have been only few studies on the separation by using liquid indium electrodes.[16,17,24,38–41]

The goal of this manuscript is to study the principal thermodynamic properties of cerium and uranium in molten 3LiCl-2KCl eutectic, solubility of cerium in liquid indium and the separation factor (SF) of U/Ce couple.

Experimental

The whole electrochemical research process was carried out in In/3LiCl-2KCl matrix. The mole ratio of molten lithium/potassium chlorides during the experiment was 3:2. Since lithium chloride is a hygroscopic salt and this fact was influenced at the accuracy of the experiments, the salt was placed in a vacuum drying furnace at a temperature 473 K for 12 h for removing the moisture of water before the investigations. Lithium chloride (>99.7%) and potassium chloride (>99.7%) were purchased from Shanghai Zhan Yun Chemical Co., Ltd. Cerium chloride heptahydrate (AR 99.99%) was purchased from Aladdin Industrial Corporation. Reagents $CeCl_3$ and UCl_4 were prepared by reaction of carbochlorination.[34]

The experiments were carried out in a three-electrode quartz glass tube under a high-purity argon atmosphere at the temperature range of 723–823 K. An inert solid molybdenum electrode and an active liquid indium electrode were used as the working electrodes. The molybdenum electrode was a wire with a diameter of 0.5 mm. The high-purity indium was placed in a micro-crucible made from corundum. The amount of indium was 2–4 g. The reference electrode was made from a corundum tube, the lower part of which had a thickness less than 0.1 mm. This was provided the ion exchange between the standard and the test electrolytes. The AgCl content in standard molten salt was 0.0039 m.f. (1.0 wt.%). Recalculation of the obtained data vs to the chlorine reference

[z]E-mail: alena_novoselova@list.ru; zhqw1888@sohu.com

electrode was carried out. The counter electrode for experiment was made of 3 mm vitreous carbon rod (SU-2000). All electrochemical data during the experiment were measured by using the PGSTAT 302 N electrochemical workstation (Autolab, Metrohm) controlled by Nova 1.8 software package. The concentration of Ce and U in molten 3LiCl-2KCl eutectic was about (2.0–3.0 wt.%) and less than 0.5 wt.%. in alloys. The following primary battery were used for measuring equilibrium electrode potentials of Ce^{3+}/Ce, (U^{4+}/U) couples (1) and for the equilibrium electrode potentials of the alloys (2) by open-circuit chronopotentiometry (OCP):

$$(-)Mo_{(s)}\ Ce,\ (U)|\text{molten salt},\ Ce^{3+},\ (U^{4+})||\text{molten salt}|\ AgCl,\ Ag(+) \quad [1]$$

$$(-)Ce,\ U(In)|\text{molten salt},\ Ce^{3+},\ (U^{4+})||\text{molten salt}|\ AgCl,\ Ag(+) \quad [2]$$

Using the OCP method it is possible to minimize the appearance of trivalent uranium ions in the melt due to the short duration of part of the experiment. In this regard, we can assume that the potential-time dependence corresponds to the quasi-equilibrium potential of the U (IV)/U couple.

After the experiments, a small amount of the alloy and a sample of solid salts were dissolved, respectively, in acid and in aqueous solutions. The concentration of cerium (uranium) in the samples was determined by the ICP-MS test.

Results and Discussion

The equilibrium electrode potential of the Me^{n+}/Me couple (where Me = Ce, U) was measured by OCP method. After deposition of a small amount of metal on the surface of inert molybdenum electrode, the value of horizontal plateau on the potential-time dependence was fixed as the quasi-equilibrium potential. In order to calculate the principal thermodynamic properties of $MeCl_n$ in molten salts, the values of the apparent standard potentials were calculated by Nernst Eq. 3. The AgCl/Ag reference electrode was used at the measurement processes. For thermodynamic calculations, it is necessary to know the values of apparent electrode potentials of Me^{n+}/Me couple vs to the reference Cl^-/Cl_2 electrode.

$$E_{Me^{n+}/Me} = E^*_{Me^{n+}/Me} + \frac{RT}{nF}\ln C_{Me^{n+}} \quad [3]$$

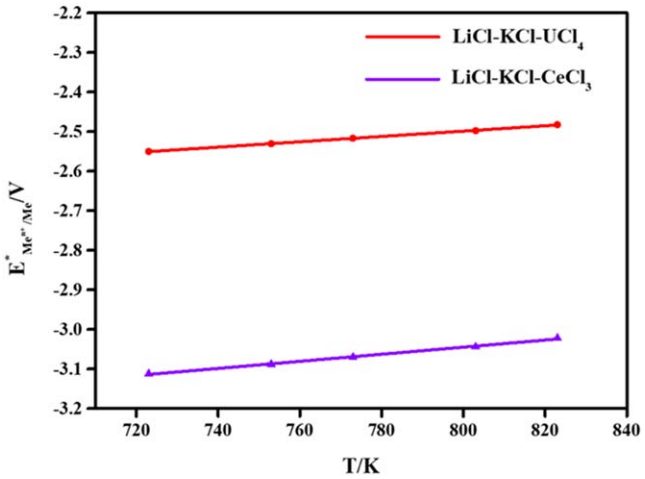

Figure 1. Variation of the apparent standard potentials $E^*_{Ce^{3+}/Ce}$ and $E^*_{U^{4+}/U}$ vs Cl^-/Cl_2 as a function of the temperature in fused 3LiCl-2KCl eutectic. The concentration of $CeCl_3$ in the solvent—2.05 wt.%; UCl_4—1.87 wt.%.

$$E^*_{Me^{n+}/Me} = E^0_{Me^{n+}/Me} + \frac{RT}{nF}\ln f_{Me^{n+}} \quad [4]$$

$$E^*_{Ce^{3+}/Ce} = E_{Ce^{3+}/Ce} - \frac{RT}{3F}\ln C_{Ce^{3+}} + E_{AgCl/Ag}\ (\text{vs } Cl^-/Cl_2) \quad [5]$$

$$E^*_{U^{4+}/U} = E_{U^{4+}/U} - \frac{RT}{4F}\ln C_{U^{4+}} + E_{AgCl/Ag}\ (\text{vs } Cl^-/Cl_2) \quad [6]$$

where $E_{Me^{n+}/Me}$ is the quasi-equilibrium electrode potential of the system, V; $E^*_{Me^{n+}/Me}$ is the apparent electrode potential of the system, V; n is the number of the exchange electrons; $C_{Ce}{}^{3+}$, $C_U{}^{4+}$ is the concentration in the melt, m.f.; $f_{Ce^{3+}}$, $f_{U^{4+}}$ is the activity coefficient of cerium (uranium).

For recalculation data of the AgCl/Ag reference electrode with the molar fraction of AgCl 0.0039 (1.0 wt.%) vs to Cl^-/Cl_2 reference electrode, the following equation was used[42]:

$$E_{AgCl/Ag}\ (\text{vs } (Cl^-/Cl_2)/V) = -1.0910 - 1.855 \cdot 10^{-4}\,T(K) \quad [7]$$

The variation between the apparent standard potential of the couples Ce^{3+}/Ce and U^{4+}/U as a function of the temperature is shown in Fig. 1. The obtained experimental data was fitted by using software Origin Pro 9.64.

$$E^*_{Ce^{3+}/Ce} = -(3.727 \pm 0.007) + (8.40 \pm 0.23) \cdot 10^{-4}T \pm 0.007\ V \quad [8]$$

$$E^*_{U^{4+}/U} = -(3.108 \pm 0.01) + (7.32 \pm 0.25) \cdot 10^{-4}T \pm 0.004\ V \quad [9]$$

When the concentration of metal ions in the molten salt does not exceed $(3–5)\cdot 10^{-2}$, the activity coefficient of Me^{n+} ($Ce^{3+}$and U^{4+}) can be regarded as a constant.[43] So, the activity coefficient γ_{MeCl_n} in the studied molten 3LiCl-2KCl eutectic could be calculated by means of the equation:

$$2.303\ RT \log f_{MeCl_n} = \Delta G^*_{MeCl_n} - \Delta G^0_{MeCl_n} \quad [10]$$

where

$$\Delta G^*_{MeCl_n} = nFE^*_{MeCl_n} \quad [11]$$

The hypothetical supercooled liquid was chosen as the reference state. $\Delta G^0_{MeCl_n}$ corresponds to the reaction between the pure compounds:

$$Me + \frac{n}{2}Cl_2 = MeCl_n \quad [12]$$

and was derived from Refs. 44, 45. The activity coefficient gives an idea of the cation complexation in molten chlorides. Based on this, it can be predicted that the chlorine complexes formation will be formed according to the following reactions:

$$Ce^{3+} + 6Cl^- = CeCl_6^{3-} \quad [13]$$

$$U^{4+} + 6Cl^- = UCl_6^{2-} \quad [14]$$

The activity coefficients of $CeCl_3$ and UCl_4 in molten 3LiCl-2KCl eutectic vs the temperature were fitted to the expressions 15–16:

$$\log f_{CeCl_3} = -0.38 - \frac{1022}{T} \pm 0.03 \quad [15]$$

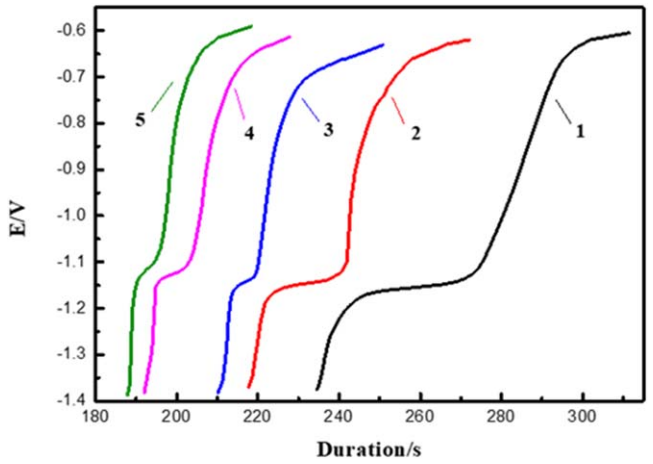

Figure 2. Dependences of potential-time 3LiCl-2KCl-UCl_4 (2.4 wt.%) melt vs Ag/AgCl RE on the liquid In WE (S = 0.38 cm^2) after short polarization at inert atmosphere. Current—80 mA; duration—20 s. Temperature: 1–723; 2–753; 3–773; 4–803; 5–823 K.

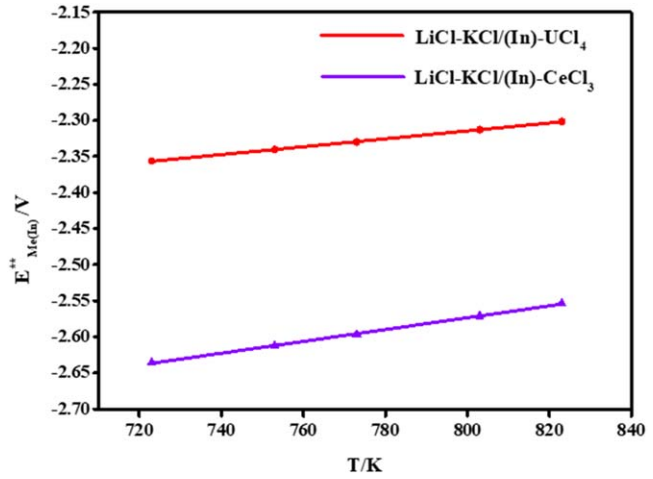

Figure 3. Variation of the apparent standard potential of the alloy $E^{**}_{Ce(In)}$ and $E^{**}_{U(In)}$ vs Cl^-/Cl_2 as a function of the temperature in molten 3KCl-2LiCl eutectic. The concentration of Ce in the alloy—0.36 wt.%. The concentration of U in the alloy—0.28 wt.%.

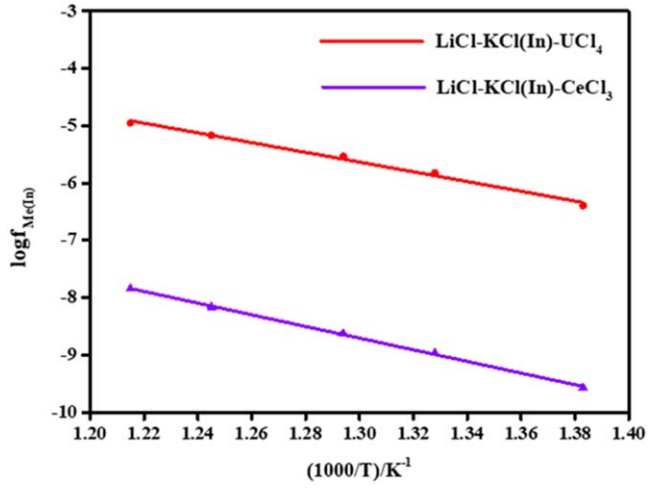

Figure 4. Variation of the activity coefficients of solid U and Ce on liquid metal (In) as a function of the temperature.

$$\log f_{UCl_4} = 3.31 - \frac{9892}{T} \pm 0.15 \quad [16]$$

The data obtained are in good agreement with those available in the literature for cerium.[29]

In order to calculate the apparent standard potential of Ce (In) and U(In) alloys, the Nernst Eq. 17 was applied.

$$E_{Me(In)} = E^0_{Me(In)} + \frac{RT}{nF} \ln \frac{a_{Me^{n+}}}{a_{Me(In)}} \quad [17]$$

or

$$E_{Me(In)} = E^0_{Me(In)} + \frac{RT}{nF} \ln \frac{C_{Me^{n+}} \cdot f_{Me^{n+}}}{x_{Me(In)} \cdot \gamma_{Me(In)}} \quad [18]$$

For the dilute dissolved metals in liquid indium, the activity coefficients of uranium and cerium are also constant.[38] Therefore, the apparent standard potential $E^{**}_{Me(In)}$ of the alloy in the liquid cathode was described by the following expression:

$$E_{Me(In)} = E^{**}_{Me(In)} + \frac{RT}{nF} \ln \frac{C_{Me^{n+}}}{x_{Me(In)}} \quad [19]$$

where Me = Ce or U; $E_{Me(In)}$ is the equilibrium potential of Me-In alloy, V; $E^{**}_{Me(In)}$ is an apparent standard potential of Me-In alloy, V; n is the number of exchanged electrons; $C_{Me^{n+}}$ is the concentration of the metal ions in solvent in mole fraction; $x_{Me(In)}$ is the concentration of the metal atoms in the alloy in atomic fraction.

The equilibrium electrode potentials of the Me-In alloys (where Me = Ce, U) was measured by OCP method. The dependences of potential-time 3LiCl-2KCl-UCl_4 (2.4 wt.%) melt vs Ag/AgCl RE on the liquid In WE (S = 0.38 cm^2) after short polarization at inert atmosphere was presented as an example in Fig. 2.

The calculated values of apparent standard potentials of alloys in fused 3LiCl-2KCl eutectic at different temperatures are presented in Fig. 3. The experimental data was fitted by using the software Origin Pro 9.64.

$$E^{**}_{Ce(III)/Ce(In)} = -(3.025 \pm 0.008) + (5.46 \pm 0.15) \cdot 10^{-4} T \pm 0.004 \text{ V} \quad [20]$$

$$E^{**}_{U(IV)/U(In)} = -(2.612 \pm 0.006) + (3.54 \pm 0.12) \cdot 10^{-4} T \pm 0.004 \text{ V} \quad [21]$$

The activity coefficients of solid Ce and U in the liquid indium can be determined by expression 22[38]:

$$\log \gamma_{Me(In)} = \frac{nF}{2.3RT}(E^*_{Me^{n+}/Me} - E^{**}_{Me(In)}) \quad [22]$$

The activity coefficients of solid Ce and U in liquid indium vs the temperature were fitted by using software Origin Pro 9.64 and presented in Fig. 4.

$$\log \gamma_{Ce(In)} = 5.11 - \frac{10682}{T} \pm 0.48 \quad [23]$$

$$\log \gamma_{U(In)} = 2.51 - \frac{6365}{T} \pm 0.40 \quad [24]$$

The calculated values of the activity coefficient are very small. This fact indicates at a strong interaction between Ce and U metals with liquid indium. Figure 4 clearly shows that the increasing of the temperature shifts the system towards more ideal behavior.[46] The obtained results of the activity coefficients of cerium in liquid indium are satisfactorily fitted with the available data in literature,

Table I. Comparison of the experimental data on the activity coefficients and solubility of lanthanides of the cerium subgroup in the system "liquid indium—molten salt" at 773 K.

Element	$\log \gamma_{Ln(In)}$	$\log x_{Ln(In)}$	References
La	−9.63	2.10	50
Ce	−8.78	−1.35	47
Ce	−8.62	−2.54	[this work]
Pr	−9.60	−2.10	51
Nd	−9.21	−2.32	52
Sm	−9.62	−1.98	53

expression 25.[47]

$$\log \gamma_{Ce(In)} = 2.41 - \frac{8650}{T} \quad [25]$$

The results of a comprehensive study of solutions of Ln compounds (4f elements) in molten salts[48] indicate the proximity of their electrochemical properties. This is due to the close values of their ion radiuses in the row from lanthanum (0.122 nm) to lutetium (0.099 nm). According to the theory of lanthanoid compression the properties of 4f elements should be change monotonously.[49] The available in the literature data for the cerium subgroup is shown in Table I. The analysis of these results shows that the lanthanides characteristics of the cerium subgroup are also close to each other within the limits of the experiment error, which is confirmed by the theory of lanthanoid compression.

The relationship between the activity, solubility and activity coefficient are described by the following expression 26[38]:

$$\log a = \log x + \log \gamma \quad [26]$$

In the above formula, α is activity; x is solubility and γ is activity coefficient.

For calculation of the activity of solid Ce in saturated Ce-In alloys containing intermetallic compounds ($CeIn_3$[54]), the Eq. 27 was used:

$$\log a = \frac{nF\Delta E}{2.3RT} \quad [27]$$

where ΔE represents the difference between the equilibrium potential of the couple ($E_{Me^{n+}/Me}$) and the equilibrium potentials of saturated alloy ($E_{Me(In)}$) in the above formula, V; n is the number of exchanged electrons.

The obtained results can be approximated by the Eq. 28 in the studied temperature range and are presented in Fig. 5:

$$\log a = 5.09 - \frac{12650}{T} \pm 0.65 \quad [28]$$

The literature data (exp. 29)[50] of the activity of cerium in liquid indium are satisfactorily adapted with the results of this work.

$$\log a = 3.97 - \frac{12230}{T} \quad [29]$$

The solubility of cerium in the liquid indium was calculated according to the expression 26. The results are presented by expression 30 and in Fig. 6. The obtained results are summarized in Table II.

$$\log x = 0.28 - \frac{2248}{T} \pm 0.05 \quad [30]$$

The results, obtained in this work are near to the literature one,[50] (exp. 31):

$$\log x = 1.56 - \frac{3580}{T} \quad [31]$$

The partial excess Gibbs energy of uranium and cerium in the liquid indium was calculated according to Eq. 33, which is described by expressions 34, 35,

$$\Delta G^{ex}_{Me(In)} = \Delta H_{Me(In)} - T\Delta S^{ex}_{Me(In)} \quad [32]$$

$$\Delta G^{ex}_{Me(In)} = 2.303RT \log \gamma_{Me(In)} \quad [33]$$

$$\Delta G^{ex}_{Ce(In)} = -203.9.65 + 97.50 \cdot 10^{-3} T \pm 3.82 \text{ kJ mol}^{-1} \quad [34]$$

$$\Delta G^{ex}_{U(In)} = -126.38 + 54.95 \cdot 10^{-3} T \pm 4.12 \text{ kJ mol}^{-1} \quad [35]$$

where ΔG^{ex} is the partial excess Gibbs free energy change, kJ mol^{-1}, ΔH is a partial enthalpy change of mixing, kJ mol^{-1}, ΔS^{ex} is a partial excess entropy change, J $mol^{-1}{\cdot}K^{-1}$.

The obtained results show a slight difference in the data of the partial enthalpy change of mixing and partial excess entropy change for Ce-In alloy ($\Delta H = -165.8$ kJ mol^{-1}; $\Delta S^{ex} = -46.1$ J $mol^{-1}{\cdot}K^{-1}$ [38]), which may be due to different conditions of the experiments. The comparison obtained data with U-In alloys also indicates to the difference ($\Delta H = -39.0$ kJ mol^{-1}; $\Delta S^{ex} = -45.2$ J $mol^{-1}{\cdot}K^{-1}$ [38]).

The reaction of the alloy formation can be generally written as:

$$[MeCl_6]^{n-} + ne + nIn = Me(In)_n + 6Cl^- \quad [36]$$

In the study of the separation of lanthanides and actinides in the spent nuclear fuel, the effectiveness of using electrochemical separation methods is usually described by the value of the distribution or separation factor. The value of the separation factor is described by Eq. 37:

$$\Theta = \frac{C_2X_1}{C_1X_2} \quad [37]$$

where C_1 and C_2 is the concentrations of metals M_1 and M_2 in the electrolyte and in the alloy (x_1, x_2). The separation factor of uranium and cerium can be written as (exp. 38):

$$\Theta = \frac{C_{Ce^{3+}}X_U}{C_{U^{4+}}X_{Ce}} \quad [38]$$

In the above expression, X_U, X_{Ce} are the uranium and cerium concentration in the liquid indium, in atomic fraction; $C_{Ce^{3+}}$, $C_{U^{4+}}$ are the concentration of Ce^{3+} and U^{4+} ions in electrolyte in mole fraction.

The separation factor was calculated by using formula 39[38] for uranium and cerium on the liquid indium:

$$\log \Theta = \frac{(n-m)FE + mFE^{**}_{Ce(In)} - nFE^{**}_{U(In)}}{2.3RT} \quad [39]$$

where $E^{**}_{Ce(In)}$ is the apparent standard potential of cerium in alloy, V; $E^{**}_{U(In)}$ is the apparent standard potential of uranium in alloy, V; m and n are the number of the exchange electrons.

Using the temperature dependence of the apparent standard potentials of cerium (20) and uranium (21) in alloys, the following expression for separation factor of uranium and cerium was obtained:

$$\log \Theta = -2.72 + \frac{4892}{T} \pm 0.05 \quad [40]$$

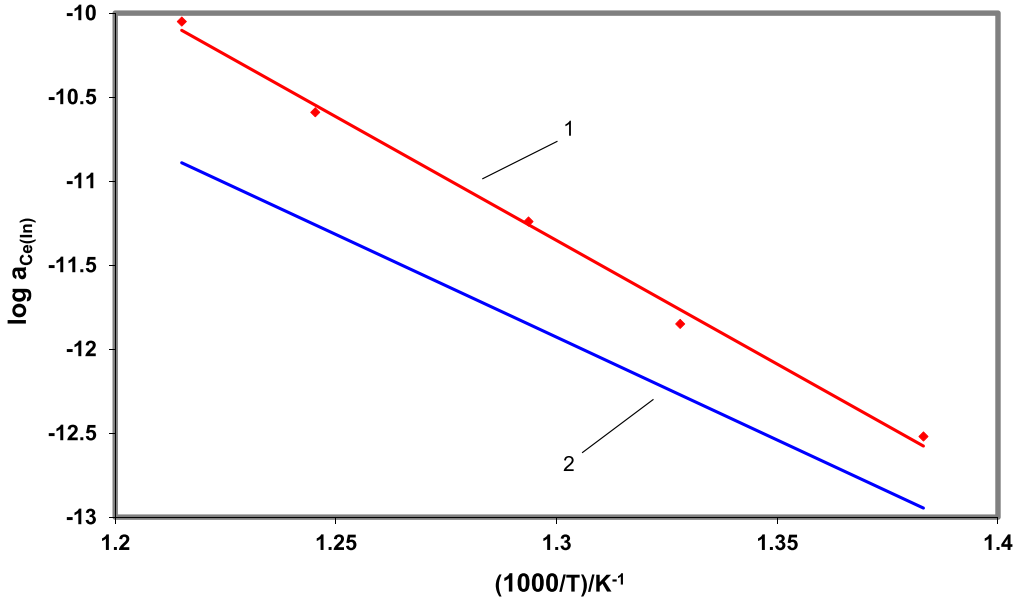

Figure 5. Variation of the activity of cerium in liquid indium as a function of the temperature. 1—Present work; 2—.[42]

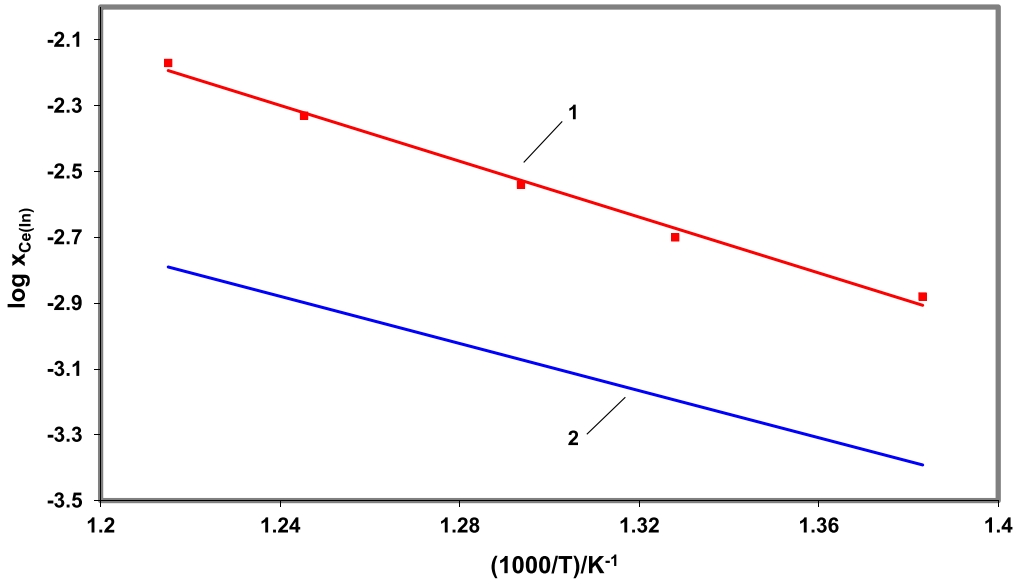

Figure 6. Variation of the solubility of cerium in liquid indium as a function of the temperature. 1—Present work; 2—.[42]

Table II. Experimental and calculated thermodynamic and solubility data of cerium in molten In/3LiCl-2KCl system at different temperatures.

T/K	$E^{eq.}_{Ce^{3+}/Ce}$/V	$E^{*}_{Ce^{3+}/Ce}$/V	$E^{eq.}_{Ce(In)}$/V	$E^{**}_{Ce(In)}$/V	log $\gamma_{Ce(In)}$	log $x_{Ce(In)}$
723	−3.235	−3.122	−2.662	−2.636	−9.67	−2.84
753	−3.208	−3.091	−2.639	−2.613	−9.09	−2.71
773	−3.182	−3.070	−2.614	−2.598	−8.62	−2.54
803	−3.175	−3.047	−2.589	−2.573	−8.26	−2.33
823	−3.147	−3.021	−2.571	−2.554	−7.84	−2.17

The separation factor of the uranium-cerium couple in the molten 3LiCl-2KCl eutectic, calculated according to the above formula, indicates that cerium will be concentrated in the molten salt phase and uranium will be deposited in the liquid metal phase. The results of calculations show that the high values of SF can be achieved only at low temperatures. Separation factor values decrease with the increasing of the temperature, due to the entropy factor. The obtained results are summarized in Fig. 7 Table III. The effect of lanthanoid compression on the separation of uranium from lanthanides can be traced.[55] It can be seen that for the cerium subgroup of lanthanides, a decrease of separation factor in the row from La to Nd is recorded.

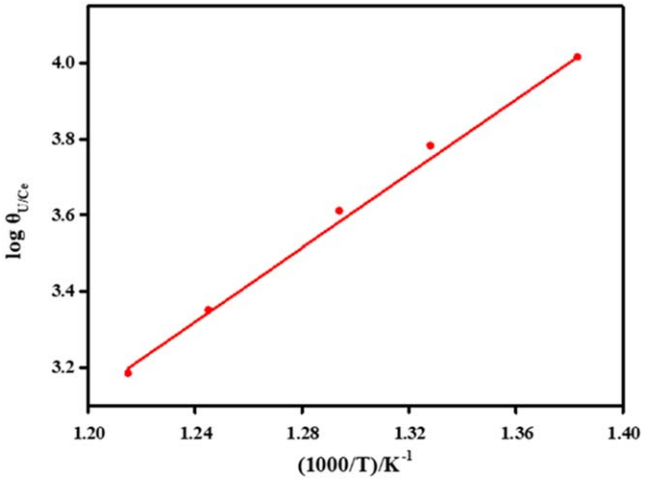

Figure 7. Variation of the separation factor of uranium from cerium on liquid metal indium as a function of the temperature.

Table III. Experimental and calculated data of uranium and separation factor Ce/U in molten In/3LiCl-2KCl system at different temperatures.

T/K	$E^{eq.}_{U^{4+}/U}$/V	$E^{*}_{U^{4+}/U}$/V	$E^{eq.}_{U(In)}$/V	$E^{**}_{U(In)}$/V	log $\gamma_{U(In)}$	log $\Theta_{(Ce/U)}$
723	−2.676	−2.550	−2.353	−2.328	−6.19	4.01
753	−2.653	−2.534	−2.339	−2.319	−5.77	3.78
773	−2.629	−2.516	−2.323	−2.305	−5.53	3.61
803	−2.611	−2.498	−2.308	−2.291	−5.16	3.35
823	−2.594	−2.482	−2.295	−2.280	−4.95	3.18

Conclusions

The electrochemical behavior of uranium and cerium on solid inert molybdenum and liquid active indium electrodes in fused 3LiCl-2KCl eutectic vs AgCl/Ag reference electrode in the temperature range of 723–823 K at inert atmosphere by open-circuit potentiometry was studied. The principal thermodynamic properties, activity and solubility of cerium and uranium were calculated. The separation factor of uranium/cerium couple on liquid indium electrodes was determined. It has been found that a lower temperature is more effective for separation actinides from lanthanides. Analysis of experimental data shows that this system is interesting in future innovative methods of nuclear waste disposal.

ORCID

Valeri Smolenski https://orcid.org/0000-0002-8303-9626
Alena Novoselova https://orcid.org/0000-0002-2338-0646
Milin Zhang https://orcid.org/0000-0001-6161-8267

References

1. T. Inoue and L. Koch, *Nuclear Engineering and Technology*, **40**, 183 (2008).
2. V. E. Komarov, V. V. Smolenski, and V. K. Afonichkin, *Melts*, **2**, 59 (2000), (in Russian).
3. M. V. Kormilitsyn, A. V. Bychkov, and V. S. Ishunin, *Global*, 782 (2003), USA.
4. J. J. Laidler, J. E. Battles, and W. E. Millar, *J. Nucl. Mater.*, **31**, 131 (1997).
5. Y. Sakamura, T. Hijikata, K. Kinoshita, T. Inoue, T. Storvick, C. Krueger, L. Grantham, S. Fusselman, D. Grimmett, and J. Roy, *J. Nucl. Sci. Technol.*, **35**, 49 (1998).
6. J. Zhang, *J. Nucl. Mater.*, **447**, 271 (2014).
7. H. P. Nawada and K. Fukuda, *J. Phys. Chem. Solids*, **66**, 647 (2005).
8. M. Iizuka, T. Koyama, N. Kondo, R. Fujita, and H. Tanaka, *J. Nucl. Mater.*, **247**, 183 (1997).
9. K. Uozumi, K. Kinoshita, T. Inoue, S. Fusselman, D. Grimmett, J. Roy, T. Storvick, C. Krueger, and C. Nabelek, *J. Nucl. Sci. Technol.*, **38**, 36 (2001).
10. K. Kinoshita, M. Kurata, and T. Inoue, *J. Nucl. Sci. Technol.*, **37**, 75 (2000).
11. G. Y. Kim, D. Yoon, S. Paek, S. H. Kim, T. J. Kim, and D. H. Ahn, *J. Electroanal. Chem.*, **682**, 128 (2012).
12. Y. Sakamura, T. Inoue, O. Shirai, T. Iwai, Y. Arai, and Y. Suzuki, *Proceedings of the International Conference on Future Nuclear Systems, GLOBAL'99* (1999).
13. T. Kato, T. Inoue, T. Iwai, and Y. Arai, *J. Nucl. Mater.*, **357**, 105 (2006).
14. T. Koyama, M. Iizuka, Y. Shoji, R. Fujita, H. Tanaka, T. Kobayashi, and M. Tokiwai, *J. Nucl. Sci. Technol.*, **34**, 384 (1997).
15. T. Murakami, Y. Sakamura, N. Akiyama, S. Kitawaki, A. Nakayoshi, and T. Koyama, *Procedia Chemistry*, **7**, 798 (2012).
16. V. Smolenski, A. Novoselova, A. Osipenko, and A. Maershin, *Electrochim. Acta*, **145**, 81 (2014).
17. V. Smolenski, A. Novoselova, and V. A. Volkovich, *J. Nucl. Mater.*, **495**, 285 (2017).
18. V. A. Volkovich, D. S. Maltsev, L. F. Yamshchikov, A. V. Chukin, V. V. Smolenski, A. V. Novoselova, and A. G. Osipenko, *J. Nucl. Mater.*, **465**, 153 (2015).
19. V. Smolenski, A. Novoselova, V. Volkovich, Y. Luk'yanova, A. Osipenko, A. Bychkov, and T. R. Griffiths, *J. Radioanal. Nucl. Chem.*, **311**, 687 (2017).
20. V. Smolenski, A. Novoselova, A. Bychkov, V. Volkovich, Y. Luk'yanova, and A. Osipenko, In:*Uranium—Safety, Resources, Separation and Thermodynamic Calculation* (IntechOpen, Rijeka) p. 109 (2018).
21. K. Yasuda, S. Kobayashi, T. Nohira, and R. Hagiwara, *Electrochim. Acta*, **106**, 293 (2013).
22. G. De Córdoba, A. Laplace, O. Conocar, J. Lacquement, and C. Caravaca, *Electrochim. Acta*, **54**, 280 (2008).
23. V. Smolenski and A. Novoselova, *Electrochim. Acta*, **63**, 179 (2012).
24. A. Novoselova and V. Smolenski, *J. Nucl. Mater.*, **509**, 313 (2018).
25. A. Novoselova, V. Smolenski, V. Volkovich, and Y. Luk'yanova, *J. Chem. Thermodyn.*, **130**, 228 (2019).
26. S. A. Kuznetsov, H. Hayashi, K. Minato, and M. Gaune-Escard, *Electrochim. Acta*, **51**, 2463 (2006).
27. K. Serrano and P. Taxil, *J. Appl. Electrochem.*, **29**, 497 (1999).
28. R. B. Prabhakara, S. Vandarkuzhali, T. Subramanian, and P. Venkatesh, *Electrochim. Acta*, **49**, 2471 (2004).
29. Y. Castrillejo, M. R. Bermejo, R. Pardo, and A. M. Martínez, *J. Electroanal. Chem.*, **522**, 124 (2002).
30. W. Lu, L. Y. Lan, L. Kui, T. S. Ling, and S. W. Qun, *Journal of Electrochemical Society*, **162**, 179 (2015).
31. L. David, C. Séverine, B. Gilles, S. Sylvie, and P. Gérard, *J. Nucl. Mater.*, **341**, 131 (2015).
32. M. Zhang, H. Y. Wang, W. Han, M. L. Zhang, Y. N. Li, Y. L. Wang, Y. Xue, F. Q. Ma, and X. M. Zhang, *Science China Chemistry*, **57**, 1477 (2014).
33. K. Liu, Y.-L. Liu, Z.-F. Chai, and W.-Q. Shi, *Journal of Electrochemical Society*, **164**, 169 (2017).
34. K. Jiang, V. Smolenski, A. Novoselova, M. Zhao, Q. Liu, H. Zhang, Y. Shao, M. Zhang, and J. Wang, *Electrochim. Acta*, **318**, 194 (2019).
35. C. H. Lee, T.-J. Kim, S. Park, S.-J. Lee, S.-W. Paek, D.-H. Ahn, and S.-K. Cho, *J. Nucl. Mater.*, **488**, 210 (2017).
36. D. S. Maltsev, V. A. Volkovich, B. D. Vasin, and E. N. Vladykin, "An electrochemical study of uranium behaviour in LiCl-KCl-CsCl eutectic melt." *J. Nucl. Mater.*, **467** (2015)956.
37. V. Smolenski, A. Novoselova, P. Mushnikov, and A. Osipenko, *J. Radioanal. Nucl. Chem.*, **311**, 127 (2017).
38. V. A. Lebedev, *Selectivity of Liquid Metal Electrodes in Molten Halide* (Metallurgiya, Chelyabinsk) p. 342 (1993), (in Russian).
39. V. Smolenski, A. Novoselova, A. Osipenko, M. Kormilitsyn, and Y. Luk'yanova, *Electrochim. Acta*, **133**, 354 (2014).
40. Y. Liu, K. Liu, L. Luo, L. Yuan, and W. Shi, *Electrochim. Acta*, **275**, 100 (2018).
41. S. Y. Melchakov, D. S. Maltsev, V. A. Volkovich, L. F. Yamshchikov, and A. G. Osipenko, *ECS Trans.*, **64**, 369 (2014).
42. L. Yang and R. G. Hudson, *J. Electrochem. Soc.*, **106**, 986 (1959).
43. M. V. Smirnov, *Electrode Potentials in Molten Chlorides* (Nauka, Moscow) p. 247 (1973), (in Russian).
44. J. Barin and O. Knacke (ed.), *Thermochemical Properties of Inorganic Substances* (Springer, Berlin) (1973).
45. HSC Chemistry 6 Software, Outotec Research Oy, Pori, Finland.
46. G. Kaptay, *Metallurgical and Materials Transactions*, **43**, 531 (2012).
47. L. F. Yamshchikov, V. A. Lebedev, and I. F. Nichkov, *Nonferrous Metallurgy*, **5**, 50 (1980), (in Russian).
48. A. Plambeck James and A. J. Bard, *Encyclopedia of Electrochemistry of the Elements* (Marcel Dekker Inc., New York and Basel)10 (1976).
49. V. Goldschmidt, *Geochemische Verteilungsgesetze Der Elemente, Skrifter Norske Videnskaps, Akad* (Oslo) (1925).

50. V. A. Degtyar, A. P. Boyanov, V. A. Vnuchkova, and V. V. Serebrennikov, *Metals*, **4**, 149 (1971), (in Russian).
51. V. A. Degtyar, A. P. Boyanov, V. A. Vnuchkova, and V. V. Serebrennikov, *J. Phys. Chem.*, **45**, 2401 (1976), (in Russian).
52. V. I. Kober, I. F. Nichkov, S. P. Raspopin, and V. M. Kuzminikh, *Termodynamics of Metal System* (Nauka, Alma-Ata) 72 (1979), (in Russian).
53. V. A. Lebedev, V. V. Efremov, and V. I. Kober, *Physical-Chemical Properties of Rare Earth Metal Alloys* (Nauka, Moscow) 96 (1975), (in Russian).
54. ASM Binary Phase Diagrams, Software, ASM International (1996).
55. V. Smolenski, A. Novoselova, V. Volkovich, A. Bychkov, Y. Luk'yanova, and A. Osipenko, *Proceedings of the International Conference on Fast Reactors and Related Fuel Cycles: Next Generation Nuclear Systems for Sustainable Development, FR 17, CN 245–35* (2017).